Marion DELILLE

LINCOLN UNIVERSITY
Christchurch, New Zealand

ENGINEERING PLACEMENT

Soil contamination with cadmium – Chemical factors affecting the sorption of cadmium by lignite and soil

Supervisor: Dr Brett ROBINSON

June – September 2012

Acknowledgement

I would like to express my sincere gratitude to Dr Brett ROBINSON, my supervisor, for giving me the opportunity to do this internship in New Zealand. He made me work on a very interesting and trainer project and he fully contributed to my integration within the team.

I would especially like to mention Hannah FRANKLIN who was always ready to help me.

Finally, I want to thank all the staff of the soil department for their hospitality and kindness. It was a pleasure to work with them. They made themselves available anytime whether it was for questions or issues about the project

Contents

About New Zealand

New Zealand is located in the south west pacific comprising two main landmasses, the South- and the North Island and numerous smaller islands including Stewart Island. All these islands come to a landmass of 268 680 square meters, which is comparable to the landmasses of the United Kingdom. The population of New Zealand is 4.3 million with 72% of the population living in the 16 main urban areas. About 15% of the population are Maori, the New Zealand indigenous people. The rest of the population are mostly European (68%) and Asian (9%) (Statistics New Zealand, 2009).

The geography of New Zealand varies a lot between the two islands. The South Island is divided through its length by the Southern Alps. The Southern Alps include 18 peaks over 3000 meters and numerous glaciers. The North Island is marked by volcanism with a volcanic plateau located in the centre of the island (Statistics New Zealand, 2009).

East Polynesians first arrived in New Zealand around 1300. They were the first settlers and are now known as the Maori. The first European to see New Zealand was Abel Tasman, a Dutch sailor, in 1642. He believed New Zealand to be part of Argentina. So he did not claim the discovery for the Netherlands. In 1769 James Cook arrived in New Zealand and claimed New Zealand for Britain. In 1840 the Treaty of Waitangi was signed. The Treaty established a British governor and recognized Maori ownership of their lands. Now New Zealand is an independent nation and part of the Commonwealth of Nations (Statistics New Zealand, 2009).

New Zealand has a developed economy with an estimated GDP of 115.624 NZD billion. The standard of living is comparable to Southern Europe with a GDP per capita of 27017 NZD in 2008. The service sector is the largest sector in the economy (68.8% of GDP), followed by manufacturing and construction (26.9% of GDP) and agriculture (4.3% of GDP) (Statistics New Zealand, 2009).

Agriculture is the main export industry together with Horticulture, Fishing and Forestry. Exports account to 24% of New Zealand’s economic output thus is very important for the country. The main agricultural export commodities are milk powder, butter and cheese and meat and edible offal (Statistics New Zealand, 2009).

About Lincoln University

Lincoln University is located on the South Island of New Zealand, about 22 km south of the city of Christchurch. There are about 4500 students enrolled at Lincoln University with students from 60 different countries. The study areas, which Lincoln University have to offer include Agriculture, Commerce, Computing, Environmental Science, Forestry, Horticulture, Hospitality, Tourism and Recreation, Sciences, Maori Studies, Landscape Architecture and Winemaking.

Lincoln University was first founded in 1878 as a School of Agriculture. The organisation of the school was linked to Canterbury College, in Christchurch. Only in 1990 Lincoln University formally separated from the now called University of Canterbury and became a self-governing national university.

Lincoln University is now governed by a council. The council is responsible for the strategic direction of the university and its performance. It also appoints the Vice- Chancellor which is responsible for the Management of the University. The Vice- Chancellor manages the key activities of the university through delegations to senior managers. The Faculties develop and give courses to students and perform research. There are three faculties and the Foundation Studies and English Language Centre. The Foundation Studies and English Language centre gives students who don't have a tertiary qualification the opportunity to study at Lincoln University. The centre also offers courses in English for academic purposes. The three faculties include the faculty of Agriculture and Life Sciences, the Faculty of Commerce and the Faculty of Environment, Society and Design. The Faculty of Agriculture and Life Sciences represents a land- based philosophy including research in the areas of nutrition and health, soil and physical sciences, applied mathematics, statistics and computational modelling, biochemistry and cell biology, microbiology, toxicology, agronomy and plant science, food science, horticulture, viticulture and oenology, farm management, ecology and conservation and plant pathology. The faculty operates three Research Farms, a vineyard, a horticultural research area, a winery and a nursery. The faculty consists of four departments (Agricultural Sciences, Ecology, Wine, Food and Molecular Biosciences and Soil and Physical Sciences). The Department of Soil and Physical Sciences comprises 19 academic staff, research officers and postdoctoral fellows and again about the same number of technical and support staff. The range of research performed in the department is extensive but has increasingly focused on environmental issues in recent years. A number of current research projects involve the measurement and modelling of solute and

microbial transport through soil. Other projects involve the measurement and modelling of gases generated within or absorbed by soils. Further examples of current projects include investigations into soil- plant rhizosphere relationships, heavy-metal contamination of soil, soil remediation and quaternary geology and paleoclimate research.

Introduction

Cadmium (Cd) is a non-essential element [1] that is readily taken up by plants and transferred through fodder and food products into animals and humans [2]. Enrichment of Cd in soils has been reported worldwide [1, 3, 4]. In a New Zealand (NZ) soil survey, Taylor et al. (2007) reported an average Cd concentration in pasture soils of 0.43 mg/kg (N = 825). This is more than double the background concentration of 0.16 mg/kg (N = 372) [5]. The main sources of Cd in these soils are phosphate fertilizers containing Cd as an impurity that originates from the phosphate rock used for their production [6]. Grazing animals take up Cd mainly via consumption of plants; intake through soil ingestion is generally lower [6, 7].

For agricultural soils, a suitable risk-mitigation technology must be low-cost and leave the soil fertile. Potentially, in situ fixation may fulfil these requirements. By applying a fixing additive to soil, Cd is transferred to a form that is less available for plant uptake. Organic (e.g. leaves, bark sawdust, peat) and inorganic (e.g. lime, hydroxyapatite) amendments can effectively reduce Cd solubility and plant uptake in contaminated soils and tailings [8], by forming insoluble organometallic compounds [9]. Lignite is discussed as a source of soil organic matter to improve soil fertility in degraded soils [10] and as a fixing additive in remediation of metal-contaminated soils [9, 11, 12]. Compared to other organic amendments such as compost, lignite is more resistant to decomposition and mineralization and shows a long-lasting activity in soil [9]. In contrast to some biochars, which also sorb Cd [13, 14], lignite is abundant worldwide and mined in great quantities. The proven recoverable world lignite resources are ca. 195 billion tonnes, with 333 million tonnes located in NZ [17, 7].

The prevalent mechanism by which metal ions are sorbed to lignite is ion exchange, but specific adsorption also plays a role [15]. Lignite contains large amounts of humic and fulvic acids [16] that have similar properties as their equivalents in soil [10]. Being a

chalcophile, Cd is expected to bind strongly to organic sulfur groups [1], R–SH, R-S-R, R-SS-R and heterocyclic S, which can be present in lignite [17]. Such binding may be important at low, biologically relevant Cd concentrations, typical for low to medium level polluted agricultural soil (e.g. Taylor (2007) [5]). In batch sorption experiments, lignite and other low rank coals effectively sorbed Cd from aqueous solution containing high Cd concentrations [15, 18-25]. Other studies found a decrease in plant uptake of Cd when Cd-contaminated soil was blended with lignite. The metal concentrations used in these treatments were usually high and resulted in reduced plant growth [9, 11, 12]. The findings of these studies nevertheless indicate that lignite application could potentially reduce the plant uptake of Cd from pasture soils with sub-phytotoxic levels of Cd contamination originating from Cd-containing P fertilizer applications.

Hypotheses and objectives

Determining the effect of Cd concentration on Cd-sorption

The threshold concentration of Cd for a soil to be classed as contaminated in most countries in 1 – 2 mg/kg. Typical concentrations in soil solution are <0.01 mg/L. Upon the addition of a sorbent such as lignite, soil solution concentrations will drop even further. Measuring such low Cd concentrations is difficult because of the detection limits of the analytical equipment and because analytical reagents and laboratory equipment can contain traces of Cd that can produce a large experimental error. In my case, I used Flame Atomic Absorption Spectroscopy (FAAS), which has a detection limit of ca. 0.05 mg/L Cd. Therefore, I conducted sorption studies using higher concentrations of Cd (10 mg/L in soil solution). This is some 1000 fold higher than occur in a contaminated soil.

As the concentration of Cd in soil increases, fewer binding sites will be available, so we would expect a relative decrease in sorption. I aimed to determine how the sorption of Cd by soil and lignite changed as a function of concentration in extracting solution.

Testing the Cd sorption-efficacy of various lignites

Previous experiments have shown that the New Vale lignite sorbed an order of magnitude more Cd than the Templeton Silt Loam. Adding this lignite to soil resulted in a disproportionate decrease in plant Cd uptake compared to other elements. We therefore hypothesised that Cd was preferentially binding to the S in the lignite. Such preferential binding is expected following the Hard-Soft-Acid-Base (HSAB) theory which states that Cd, a soft Lewis acid, should preferentially bind to soft bases such as S.

To determine whether a high-sulphur coal (Millerton) and high-sulphur lignite (Charleston) would sorb more Cd that the low-sulphur lignite (Newvale) compared to an agricultural soil (Lismore stony silt loam)

Comparative sorbtive capacities of New Vale lignite and soil in nitrates of magnesium, calcium, potassium and lithium

There is debate as to whether Cd is bound to soil via CEC or specific adsorption. Competing ions of the s-block elements do not normally bind via specific adsorption and would therefore not be likely to significantly reduce the specific adsorption of Cd. In contrast, such ions would be expected to have a large effect on the outersphere binding of Cd via cation exchange. Table 1 shows the charge / hydrated radii for the major cations in soil, which determines the binding selectivity of the ions in cation exchange reactions. Thus selectivity of the ions for CEC would follow the trend Pb > Ca > Zn > Mg > Cd > K > Na > Li.

Table 1: Charge and hydrated ionic radii of Cd and competing cations Ca, and Zn.

Elements	Charge of ion	Ionic Radius hydrated (pm)	charge / hydrated radius
Pb	2+	401	4.99×10^{-3}
Ca	2+	412	4.85×10^{-3}
Cd	2+	426	4.69×10^{-3}
Mg	2+	428	4.67×10^{-3}
Zn	2+	430	4.65×10^{-3}
K	1+	331	3.02×10^{-3}
Li	1+	382	2.62×10^{-3}

Radii of unhydrated (first value) and hydrated (second value) ions from Volkov, A. G., S. Paula, and D. W. Deamer, Two mechanisms of permeation of small neutral molecules and hydrated ions across phospholipid bilayers, Bioelectrochem. Bioenergetics 42:153-160, 1997 (taken in turn from Volkov and Deamer (Eds.), Liquid-liquid interfaces, CRC Press, Boca Raton, FL, 1996; Gourary and Adrian, Solid State Phys. 10:127, 1960; Conway, Ionic hydration in chemistry and biophysics, Elsevier, New York, 1981).

Therefore, if we use molar equivalent strengths of Ca, Mg, K and Li as ambient solutions for the soil / lignite sorption experiments, we would hypothesise that Cd sorption would increase Ca < Mg < K < Li.

I aimed to elucidate the effect of changing the ambient ion on the adsorption of Cd by the New Vale lignite and by soil.

Sorption of other ions by lignite

Simmler (2012) showed that lignite added to soil reduced the plant uptake of Cd more than it changed the plant uptake of other elements. I aimed to determine the sorption of Cu, Zn, Pb and Ni by soil and lignite at molar equivalent concentrations (89 µM). This equates to 10 mg Cd /L, 5.8 mg Zn /L, 18.5 mg Pb /L, and 5.6 mg Cu /L.

Experimental

Materials

Powdered lignite (AP < 200 µm) mined in the New Vale open cast mine in Southland (NZ) was provided by Solid Energy New Zealand Ltd. The lignite was obtained from the W7 rider seam, which is low calorific value lignite ~14.5 MJ/kg, compared to the main W6 seam that is mined for thermal coal (~15.5 MJ/kg). The lower calorific value is due to partial oxidation of the W7 seam as this rider seam is shallower and closer to ground level. A pasture soil from Lincoln University's Ashley Dene Farm (Lismore Stony Silt Loam) was used as a comparison. The properties of the soils and lignites are given in Table 2.

Table 2: Physicochemical properties for the soil and lignites used in these experiments. Values in brackets represent standard error (SE) of the mean. (N = 3 when SE is given; N = 1 when no SE is given). All units are in mg/kg unless otherwise indicated.

	Lismore Stony Silt Loam	New Vale	Millerton	Charleston
moisture (%)		**38**		
clay/silt/sand (%)		**< 200 µm†**	**< 200 µm†**	**< 200 µm†**
pH (H_20)		**5.6**		
CEC (meq/100g)		**11.9**	**n.d**	**n.d.**
C (%)		**2.4**	**n.d**	**n.d.**

N (%)	**0.26**	**n.d**	**n.d.**
P	**784**	**n.d**	**n.d.**
S	**266**	**n.d**	**n.d.**
Ca	**3037**	**n.d**	**n.d.**
Mg	**802**	**n.d**	**n.d.**
K	**1438**	**n.d**	**n.d.**
Cd	**0.2**	**n.d**	**n.d.**
Zn	**35**	**n.d**	**n.d.**
Cu	**5.7**	**n.d.**	**n.d.**
Pb	**7.7**	**n.d.**	**n.d.**

Batch sorption experiments

The soils used for the experiments were dried and passed through a 2 mm nylon sieve. The lignites were ground using a morter and pestle and dried at 105 oC until a constant weight was obtained. The moisture content of the lignite was determined.

All sorption experiments were conducted using 40 ml centrifuge tubes with 3 replicates per treatment.

The tubes were continuously agitated for 2 hours on an end-over-end shaker in order to reach sorption equilibrium (determined in a previous experiment). The pH of the slurry was measured after shaking. The tubes were centrifuged for 10 min at 3300 rpm. The supernatant was decanted and filtered through Whatman 52 filter paper (pore size 7 μm). Solution element concentrations were measured by Flame AAS (Shimadzu AA6200).

Experiment 1: Two grams of lignite or soil were added to 20 ml 0.05 M $Ca(NO_3)_2$ (BDH AnalaR $Ca(NO_3)_2x4H_2O$) solution spiked with 0, 1, 3, 10, 30, 100 and 300 mg/L Cd (BDH AnalaR $3Cd(SO_4)x8H_2O$).

Experiment 2: The solution pH was adjusted to values ranging from (3.4) to (7.4) after addition of the sorbent by using KOH (BDH AnalaR KOH) to decrease or increase pH, respectively. Centrifuge tubes containing solutions without soil or lignite were prepared as a control for each Cd concentration to determine the extent of any Cd sorption by the tubes or filter papers. The results indicated that such sorption was negligible.

Experiment 3: Extractions were conducted using solutions of 0.05 M Mg(NO3), 0.1 M KNO3, and 0.1 M LiNO3 containing 10 mg/L. Note that the concentrations of the Group I salts were double that of the Group II salts to give the same concentration of positive charge.

Experiment 4: Extractions in 0.05 M MgNO3 and 0.05M Ca(NO3)2 were conducted using molar equivalent concentrations (89 mMol) of Cd, Ni, Cu, Pb, Zn. Stock solutions were prepared for each element (Table 3)

Table 3. Concentrations, masses and volumes of the stock solutions that were prepared for each treatment.

	mg/L	mMol	Ar	Mr (salt)	g required for 100 mL soln
Cd	2000,00	17,79	112,41		0,45
Cu	1130,60	17,79	63,55	249,68	0,44
Ni	1044,26	17,79	58,69	290,81	0,52
Pb	3686,47	17,79	207,20	331,21	0,59
Zn	1163,41	17,79	65,39	287,54	0,51

Results and discussion

Experiment 1

Fig. 1 shows the sorbtion of Cd by lignite and soil as a function of Cd in the ambient solution. The sorbed concentration increased according to the function:

$$S=aC / (1+C+b) \qquad \text{Eqn 1.}$$

Where *S* is the sorbed Cd concentration (mg/kg), *C* is the concentration in soil solution (mg/L), *a* is the maximum concentration able to be bound by the material (mg/kg) and *b* is a decay constant that determines how rapidly *a* is reached.

Table 4. The maximum concentration of Cd able to be sorbed by lignite and the Lismore stony silt loam as a percentage of CEC.

	Lignite	Lismore stony silt loam
CEC ($cmol_{(+)}$/100g)	44.8	11.9
a (mg/kg)	5502	1379
a ($cmol_{(+)}$/100g)	9.8	2.5
a as % of CEC	22%	21%
b (dimensionless)	52	42

Note that mg/kg was converted to $cmol_{(+)}$/100g assuming all attached to the soil was Cd(II).

Table 4 shows the maximum concentration of Cd able to be sorbed by the material as a function of CEC. The lignite could potentially sorb 4 fold more Cd than the soil. In both cases the value of *a* was around one fifth of the CEC of the material. It would be interesting to test this ratio for other materials to determine whether this is a constant, in which case the Cd sorption potential could be simply determined by measuring CEC.

The results show that at an initial concentration of 10 mg/kg in solution, the value of KD was around 75% of the value when an initial concentration of 1 mg/kg was used, for both the lignite and the soil. This indicates that our result may provide a somewhat conservative estimate of the Cd sorption potential of lignite under field conditions, where the sorbed Cd concentration will be some 100-fold lower.

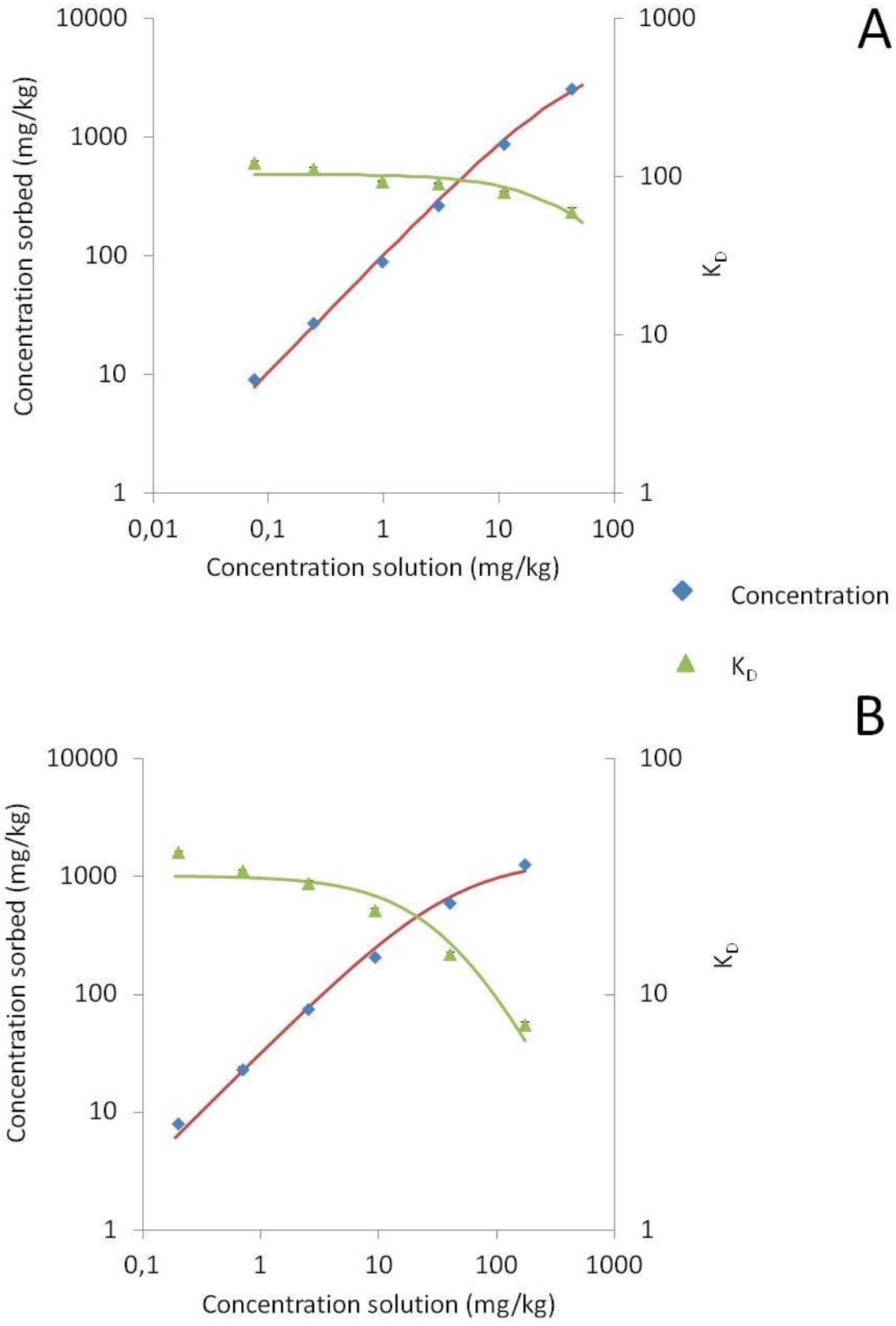

Fig. 1. Sorbed [Cd] as a function of solution [Cd] for lignite (A) and the Lismore fine sandy loam (B). The sorbed / solution concentration quotient (K_D) is shown on the secondary axis. Error bars represent the standard error of the mean (n=3

Experiment 2

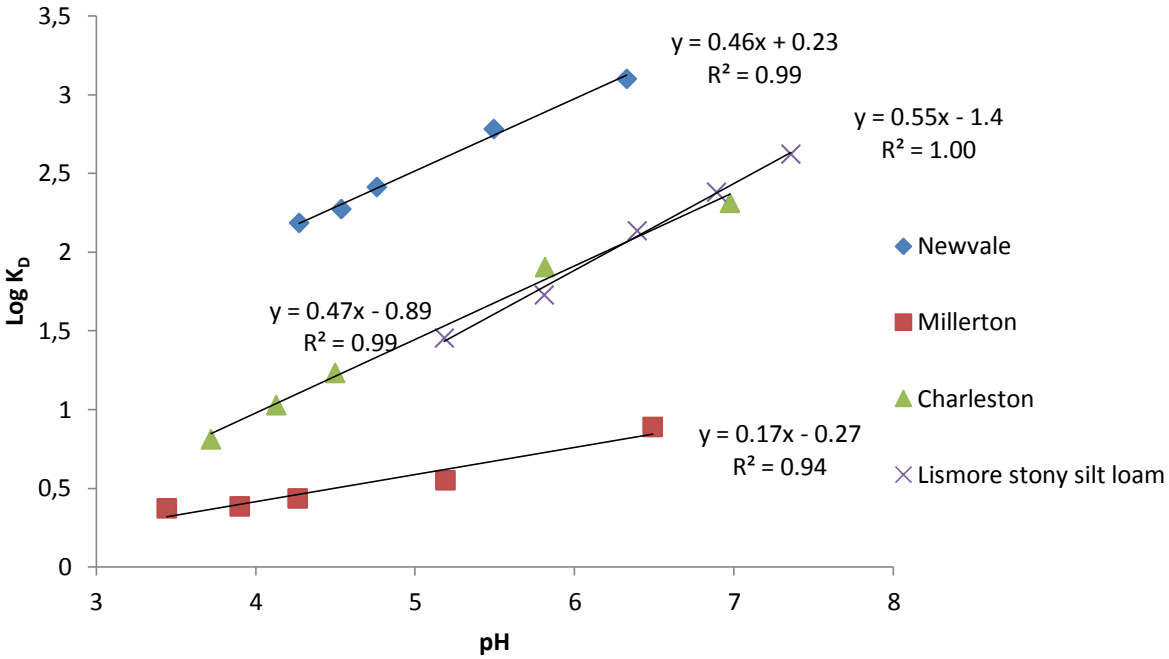

Fig.2 Log K_D (sorbed [Cd] / solution [Cd]) vs pH for three coals and an agricultural soil. Each point represents the average of three measurements. Standard errors (not shown) were <5%.

Fig. 2 shows that only the New Value lignite sorbed significantly more Cd than the agricultural soil. This indicates that of the lignites tested, only the Newvale effectively sorbed Cd from solution.

We did not test the Cation Exchange Capacity of the Millerton or Chareston coals. We therefore not comment directly on the efficacy of the sulphur that the contain on binding Cd. Nor do we know the speciation of the sulphur in each coal. For examples thiols would be expected to form more stable complexes with Cd than diphenylthiols (Reference).

It is possible that upon weathering in soil, more functional groups would form on the coals. Therefore, the sorbtive capacity of the Millerton and Charleston coals could increase. This could be the subject of further investigation.

Experiment 3

Fig. 3 shows the Cd sorption by soil and lignite in the nitrates of the above mentioned s-block elements. The results indicate that there is a profound effect of the ambient ion in the Cd sorption by both the lignite and the soil. This indicates that, in the extracting solutions at least, CEC is the dominant process by which Cd is binding to the soil and the lignite. The results shown in Fig. 3 are consistent with those expected based on the charge/hydrated radius quotients of the other cations (Table 1). These experiments do not reveal whether specific adsorption occurs over a longer period in soil. While specific adsorption of Cd may occur, it would not be expected to be as strong as transition metal ions with partially-filled d-orbitals because of the lack of Ligand Field Stabilisation Energy in the d^{10} electron configuration of Cd^{2+}.

While both soils and lignite sorb more Cd at higher pH, the results indicate that the effect of liming may be offset by the introduction of competing ions, especially Ca, which displace Cd from charged surfaces thereby resulting in increased mobility. A potential solution may be to lime with potash, which is rich in potassium and has lesser concentrations of Ca.

We did not test the effect of changing the ionic strength on Cd sorption. Other studies (REF) have shown that increasing the ionic strength decreases the sorption of cations because of increased competition for a limited number of exchange or binding sites. This has implications for the management of Cd-contaminated soils: the use of saline irrigation water or overzealous use of mineral fertilisers may increase the solubility of Cd and may result in increased plant uptake. Furthermore, other studies (REF – McLaughlin Hammon), have shown that in saline soils, Cd is complexed by Cl and the chloride complexe can be taken up by plants.

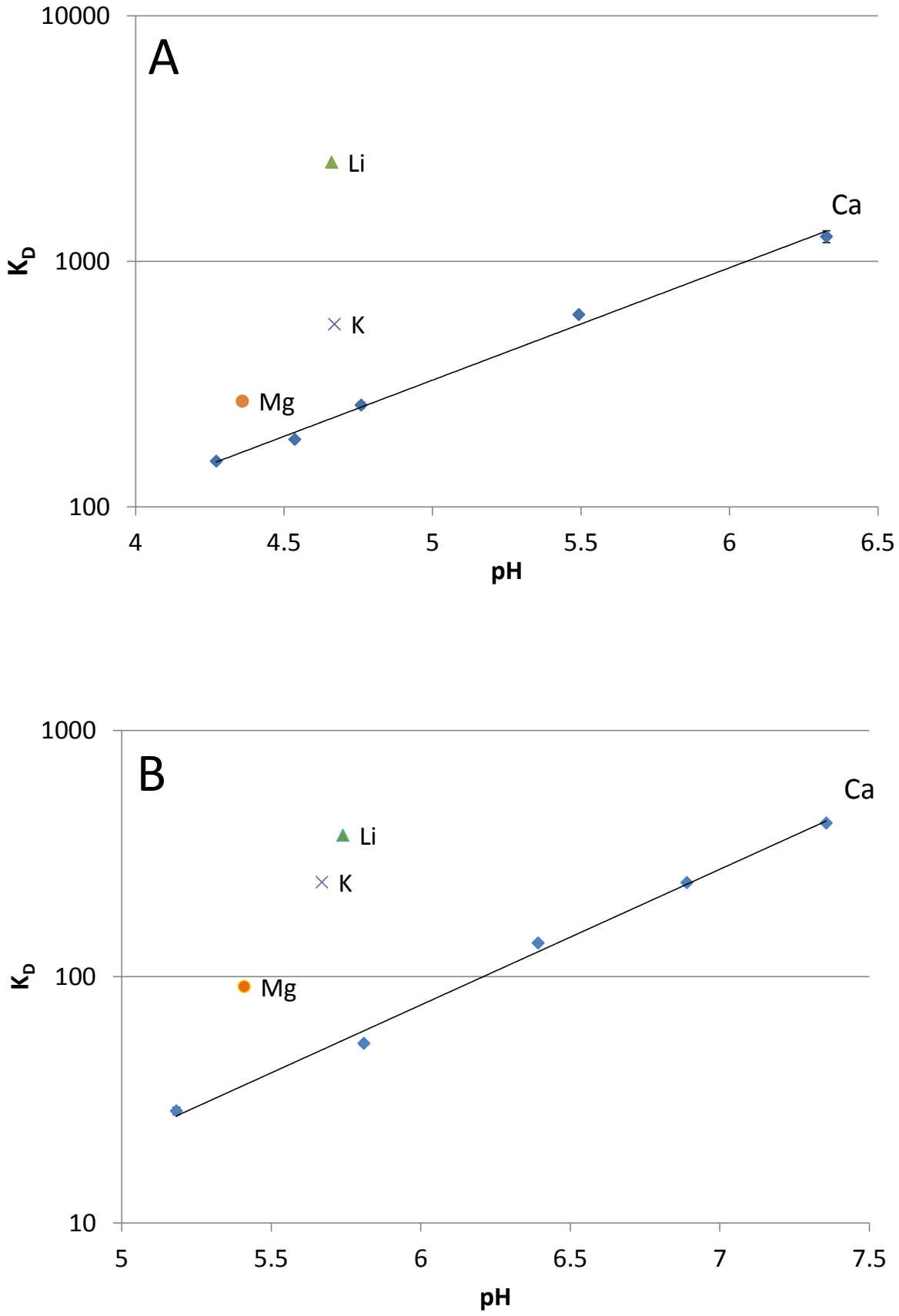

Fig. 3. Sorption of Cd by Newvalue lignite (A) and the Lismore stony silt loam (B) in nitrates of Ca, Mg, K, and Li. Points represent the average of three replicates. Standard errors were <5%.

Experiment 4

Fig. 4 shows the relative sorption of selected metals by lignite and soil in $Ca(NO_3)_2$ and $Mg(NO_3)_2$. Both the lignite and the soil sorbed metals in the order Pb>Cu > Cd≈ Ni >Zn. There were significant differences between the K_D values in the two extracting solutions (Fig. 3 A & B). Sorption was generally higher in the $Mg(NO_3)_2$ compared to the $Ca(NO_3)_2$. However, the influence of the extracting solution was greater on Cd and Pb than on Ni, Zn and Cu. These differences may be explained by the specific adsorption of Ni and Cu, a process that is less affected than cation exchange by the presence of Ca or Mg. As in Experiment 2, these results indicate that cation exchange, rather than specific adsorption, may be responsible for the immobilisation of Cd in soils amended with lignite.

The results indicate that the difference in sorbtion between the soil and the lignite was far greater for Cd than for Zn. This is consistent with the findings of Simmler (2012), who found that the influence of lignite addition to pasture was greater on Cd than on Zn. These results have important implications for the management of agricultural soils. Whereas Cd is a non-essential element that can endanger human health, Zn is an essential element. Some 25% of humanity suffer from a Zn deficiency. Therefore, lignite may find potential use as in biosolids-amended soils, where the biosolids result in increased Zn uptake but can also introduce significant amounts of Cd.

Fig. 4 indicates that while both lignite and soil strongly sorbed Pb, there was little difference in sorption between the soil and the lignite in $Ca(NO_3)_2$. Most soil contaminated with Pb are treated with lime to raise the pH. Therefore, it is unlikely that lignite will have a significant positive effect on the immobilisation of Pb in contaminated soil.

There were large differences between the soil and the lignite in the sorption of Cu, both in the $Ca(NO_3)_2$ and $Mg(NO_3)_2$. At normal soil concentrations, plants actively take up Cu (Reid and Hays, 2003) and can lessen the effect of reduced Cu in soil solution. However, in soils contaminated with Cu, such as most vineyards in France, lignite may effectively reduce the phytotoxicity of Cu and improve soil function. This warrants further research.

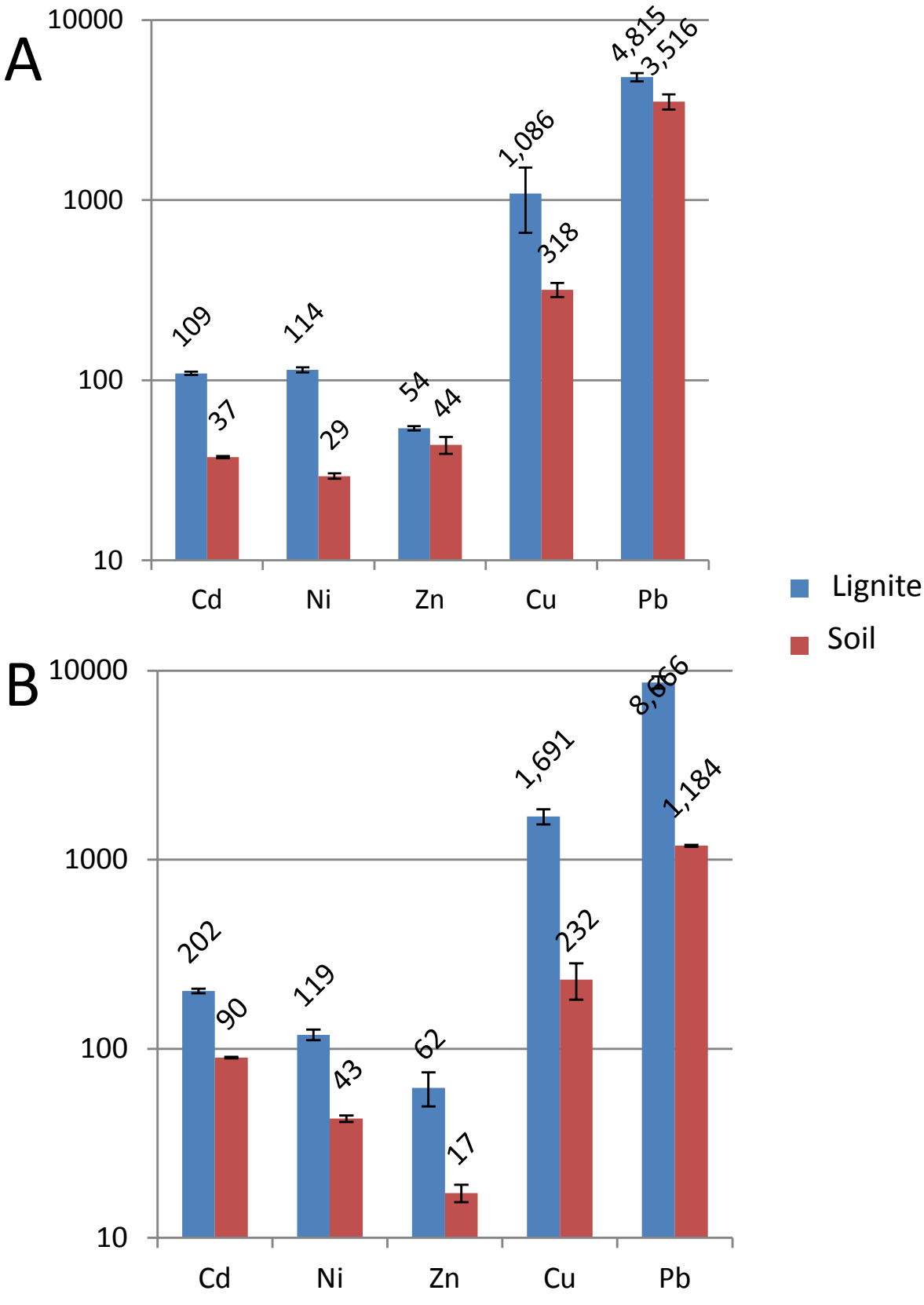

Fig. 4. Values of K_D (sorbed / solution concentration coefficient) for selected metals in $Ca(NO_3)_2$ (A) and $Mg(NO_3)_2$ (B). Bars represent the standard error of the mean (n=3).

Conclusion

Only the New Vale lignite sorbed significantly more Cd than an agricultural soil. This indicates that not all lignites will be suitable for the remediation of Cd-contaminated soils. Cadmium-sorbtion by the high-sulphur coals was over an order of magnitude lower than the low-sulphur New Vale lignite. This is inconsistent with the hypothesis that sulphur binding is the most important mechanism for Cd immobilisation in lignite. The sorption capacity of the New Value lignite and that of the Lismore Stony Silt Loam was ca. 20% of the CEC. Sorption increased exponentially upon increasing pH for all materials. Cadmium-sorption was reduced in the presence of Ca. This indicates that raising the pH of a Cd-contaminated soil using Ca-based limes may be less effective than using other liming agents such as potash (or coal ash). The New Vale lignite sorbed significantly more Cd than Zn, indicating that lignite may have a role in improving the Cd: Zn in crop plants. Our results indicate that CEC is more important than specific adsorption for the immobilisation of Cd in contaminated soils.

Future work could involve screening a suite of lignites for Cd sorption. A first estimation of the likely efficacy in this regard could be made by measuring their CEC. A critical and as yet unanswered question is how the sorbtive properties of lignite change once the material is added to soil. This requires long-term incubation experiments.

Personal conclusion

Personally, this internship has given me the opportunity to benefit from a great experience abroad. It helped me improve my English but also made me discover a new culture and taught me how to be independent in both my personal and professional life.

The project assigned during the placement was also a good experience for me because I worked on a current topic which I had no knowledge at the beginning.

References

1. Kabata-Pendias, A. and A.B. Mukherjee, *Trace elements from soil to human*. 2007, Berlin Springer.
2. Cadmium Working Group, *Cadmium and New Zealand Agriculture and Horticulture: A Strategy for Long Term Risk Management*. 2011, Ministry of Agriculture and Forestry Wellington.
3. Hooda, P.S., ed. *Trace elements in soils*. 2010, Wiley: Chichester.
4. Kabata-Pendias, A. and H. Pendias, *Trace elements in soils and plants*. 2001, Boca Raton: CRC Press.
5. Taylor, M., et al., *Soil maps of cadmium in New Zealand*. 2007, Ministry of Agriculture and Forestry: Wellington.
6. Loganathan, P., et al., *Fertiliser contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: a review*. Australian Journal of Soil Research, 2003. **41**(3): p. 501-532.
7. Lee, J., et al., *Accumulation of cadmium with time in Romney sheep grazing ryegrass white clover pasture: Effect of cadmium from pasture and soil intake.* Australian Journal of Agricultural Research, 1996. **47**(6): p. 877-894.
8. Guo, G.L., Q.X. Zhou, and L.Q. Ma, *Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: A review.* Environmental Monitoring and Assessment, 2006. **116**(1-3): p. 513-528.
9. Pusz, A., *Influence of brown coal on limit of phytotoxicity of soils contaminated with heavy metals.* Journal of Hazardous Materials, 2007. **149**(3): p. 590-597.
10. Kwiatkowska, J., M.R. Provenzano, and N. Senesi, *Long term effects of a brown coal-based amendment on the properties of soil humic acids.* Geoderma, 2008. **148**(2): p. 200-205.
11. Ciecko, Z., et al., *Effect of organic matter and liming on the reduction of cadmium uptake from soil by triticale and spring oilseed rape.* Science of the Total Environment, 2001. **281**(1-3): p. 37-45.
12. Skłodowski, P., A. Maciejewska, and J. Kwiatkowska, *The effect of organic matter from brown coal on bioavailability of heavy metals in contaminated soils*, in *Viable Methods of Soil and Water Pollution Monitoring, Protection and Remediation*, I. Twardowska, et al., Editors. 2006, Springer: Dordrecht. p. 299-307.
13. Beesley, L. and M. Marmiroli, *The immobilisation and retention of soluble arsenic, cadmium and zinc by biochar.* Environmental Pollution, 2011. **159**(2): p. 474-480.
14. Park, J.H., et al., *Biochar reduces the bioavailability and phytotoxicity of heavy metals.* Plant and Soil, 2011. **348**(1-2): p. 439-451.
15. Pentari, D., et al., *Sorption properties of low calorific value Greek lignites: Removal of lead, cadmium, zinc and copper ions from aqueous solutions.* Journal of Hazardous Materials, 2009. **168**(2-3): p. 1017-1021.
16. Pehlivan, E. and G. Arslan, *Removal of metal ions using lignite in aqueous solution - Low cost biosorbents.* Fuel Processing Technology, 2007. **88**(1): p. 99-106.
17. William H, C., *The chemical forms of sulfur in coal: a review.* Fuel, 1994. **73**(4): p. 475-484.

18. Havelcova, M., et al., *Sorption of metal ions on lignite and the derived humic substances.* Journal of Hazardous Materials, 2009. **161**(1): p. 559-564.
19. Karabulut, S., et al., *Cadmium (II) and mercury (II) removal from aquatic solutions with low-rank Turkish coal.* Separation Science and Technology, 2001. **36**(16): p. 3657-3671.
20. Burns, C.A., et al., *Cd(II) binding by particulate low-rank coals in aqueous media: sorption characteristics and NICA-Donnan models.* Journal of Colloid and Interface Science, 2004. **278**(2): p. 291-298.
21. Jochova, M., et al., *Removal of heavy metals from water by lignite-based sorbents.* Fuel, 2004. **83**(9): p. 1197-1203.
22. Pehlivan, E. and G. Arslan, *Comparison of adsorption capacity of young brown coals and humic acids prepared from different coal mines in Anatolia.* Journal of Hazardous Materials, 2006. **138**(2): p. 401-408.
23. Pehlivan, E., A. Richardson, and P. Zuman, *Electrochemical investigation of binding of heavy metal ions to Turkish lignites.* Electroanalysis, 2004. **16**(16): p. 1292-1298.
24. Janos, P., et al., *Removal of metal ions from aqueous solutions by sorption onto untreated low-rank coal (oxihumolite).* Separation and Purification Technology, 2007. **53**(3): p. 322-329.
25. Lao, C.X., et al., *Sorption of Cd(II) and Pb(II) from aqueous solutions by a low-rank coal (leonardite).* Separation and Purification Technology, 2005. **45**(2): p. 79-85.

Abstract

Soil contamination with cadmium (Cd) occurs worldwide as a result of the application of Cd-rich phosphate fertilisers and sewage sludge as well as industrial emissions. Plants take up relatively high concentrations of Cd from soil, leading to breaches of food safety standards and facilitating the entry of this toxic element into the food chain. A potential solution may be the use of lignite, a low-calorific value coal, as a soil amendment. Previous studies have shown that the addition of just 1% lignite to a silt loam reduced plant Cd uptake by 30% while not detrimentally affecting biomass or the uptake of other essential nutrients. It was hypothesised that the disproportional effect on plant Cd uptake may be due to S-containing functional groups that preferentially bind Cd. Using batch experiments, I tested whether high-S containing lignites were more effective at sorbing Cd. I also tested the effect of competing ions on the sorption of Cd and other elements. I found that the high S lignites were not effective in sorbing Cd. Cadmium sorption was greater at high pH. The presence of Ca greatly reduced Cd sorption by lignite, indicating that agents other than lime should be used to increase soil pH on Cd contaminated soils. Cadmium sorption by lignite was significantly greater than Zn sorption. Future work should include incubation experiments to determine how the sorbtive properties of lignite change over time.

Résumé

La contamination des sols par le cadmium (Cd) se produit dans le monde entier à la suite de l'application d'engrais phosphatés riches en Cd et les boues d'épuration ainsi que les émissions industrielles. Les plantes absorbent des concentrations relativement élevées de Cd dans le sol, ce qui conduit à des violations des normes de sécurité alimentaire et facilite l'entrée de cet élément toxique dans la chaîne alimentaire. Une solution possible pourrait être l'utilisation du lignite, le charbon de faible valeur calorifique, comme amendement de sol. Des études antérieures ont montré que l'ajout de seulement 1% de lignite au "slit sloam" réduit l'absorption de Cd dans les plantes de 30% sans altérer la biomasse ni l'absorption d'autres éléments nutritifs essentiels. Il a été émis l'hypothèse que l'effet disproportionné sur l'absorption de Cd dans les plantes peut être dû à des groupes fonctionnels contenant du souffre qui se lient préférentiellement au Cd. En utilisant des expériences en batchs, j'ai testé si les lignites contenant un fort pourcentage en souffre étaient plus efficaces pour l'absorption du cadmium. J'ai aussi testé l'effet d'ions concurrents sur l'absorption du Cd ainsi que sur celle d'autres éléments. J'ai pu observer de mes expériences que les lignites contenant beaucoup de souffre n'absorbaient pas de Cd, que l'absorption du Cd est plus importante à pH élevé et que la présence de calcium réduit considérablement l'absorption du Cd par le lignite, ce qui indique que des agents autres que la chaux doivent être utilisés pour augmenter le pH du sol sur des sols contaminés par le Cd. Et enfin, j'ai pu voir que l'absorption du Cd par le

lignite était significativement plus élevée que l'absorption du zinc. Les futurs travaux devraient inclure des expériences d'incubation pour déterminer comment les propriétés d'absorption du lignite change au cours du temps.